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INVESTIGATION OF A PROPRIETARY RAPID-SETTING CEMENTITIOUS MATERIAL

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PREFACE

The investigation reported herein was authorized by the first indorsement dated 7 October 1959 from the Office, Chief of Engineers, to a letter dated 2 September 1959 from the U. S. Army Engineer Waterways Experiment Station, subject, "Project Plan for Exploratory Studies of...[a proprietary rapid-setting cementitious material]." This investigation forms a part of the Civil Works Investigations Program of the Corps of Engineers, Item 614, "Research on Properties of Cementitious Materials." The work was conducted at the Concrete Division, Waterways Experiment Station (WES), under the direction of Mr. Thomas B. Kennedy. Mr. Kenneth L. Saucier was project leader. This report was prepared by Mr. Saucier and Mr. Bryant Mather. Col. Edmund H. Lang, CE, was Director and Mr. J. B. Tiffany was Technical Director of the Waterways Experiment Station during the conduct of this investigation and the preparation of this report.

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SUMMARY

A limited investigation of a proprietary, rapid-setting, cementitious material, both in the forms of a "field mix" and an "additive," indicated the following:

a. The X-ray pattern and chemical analysis showed the additive to consist of calcium sulfate hemihydrate (plaster of Paris) and clay (kaolinite); however, the set controller of the plaster was not identified.

b. The time of setting was somewhat variable, depending upon the amount of water used. For the best hand-placeable mixtures, the initial set would likely occur in a range between 5 and 15 min. Apparently the setting time (adjustable up to 25 min) referred to in the manufacturer's literature would be adjusted by the addition of water, and a fairly thin mixture would be required for hand placeability at 25 min age.

c. The small amount of test data shows the material to be reasonably certain of reaching the following compressive strengths: 100 psi at 1 hr, 2000 psi at 1 day, 4000 psi at 7 days, and 5000 psi at 28 days. The 1-day strength agrees with the manufacturer's claim, but the 28-day strength did not attain the advertised 6000 psi, apparently due to the water content. Since the amount of water used is very critical, the driest possible mix, as dictated by the setting time and workability, should be selected.

d. In order to determine sulfate resistance, two types of mortar-bar tests were made: lean bars stored in sulfate solution, and bars with added sulfate stored in water. The amount of expansion of the mortar bars indicated the sulfate susceptibility of mixtures made with the additive and of control mixtures. The lean mortar-bar test showed the additive to cause approximately three times as much expansion as exhibited by the control mixture, whereas bars with sulfate added showed almost equal expansion of the additive and two control mixtures up to 28 days age. Tests of additional mortar bars which contained the additive and cements having 12 and 6% C_3A contents showed that the cement of lower C_3A content produced less mortar-bar expansion than did the higher C_3A cement when the bars were stored in water up to 28 days. Mixtures containing this material should not be used in situations where they would be exposed to moisture in service unless they are made with sulfate-resistant (Type V) portland cement.

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KEY

Manufacturer	Symbol	Product
International Speed-Crete Research Corp. Fort Lauderdale, Florida	AD-110	"Speed-Crete" field mix
	AD-110-A	"Speed-Crete" additive
	AD-110-A(2)	"Speed-Crete" additive
Mississippi Valley Cement Co. Redwood, Mississippi	RC-449	Type I portland cement
Canada Cement Co. Montreal, Canada	RC-167	Type I portland cement
Lone Star Cement Co. Birmingham, Alabama	RC-452	Type II portland cement
Greene Brothers Sand and Gravel Co. Georgetown, Mississippi	CRD-S-4(15)	Natural siliceous sand

INVESTIGATION OF A PROPRIETARY, RAPID-SETTING CEMENTITIOUS MATERIAL

PART I: INTRODUCTION

Purpose of Investigation

1. The purpose of this investigation was to make a preliminary evaluation of a proprietary, rapid-setting, cementitious material for possible use by the Corps of Engineers, especially in the repair of elements of construction in marine exposures.

Properties Claimed for Material

2. Literature provided by the manufacturer of the cementitious material investigated states that:

- a. The material is available both for use as an additive, and combined with sand and cement into a "field mix." The mixture contains the proportions of sand, cement, and additive recommended by the manufacturer and is ready for use when mixed with water.
- b. The mixture can be placed either by spraying in fluid grout form or by hand-packing a stiffer mixture.
- c. When the mixture is placed under water a cloud will result, but it will in no way injure the water for drinking.
- d. Although mixing the field mixture with water is easy for the average laborer, a special procedure must be used to secure a uniform mixture.
- e. No resin, polyvinyl acetate, nor any other synthetic materials are used in the additive.
- f. The setting time can be adjusted up to 25 min.
- g. Laboratory tests indicate that the field mixture after 24 hr has an ultimate compressive strength in excess of 2000 psi and after 48 hr of 2500 psi. In 3 to 5 days it can top 3000 psi, and at 28 days will exceed 6000 psi.
- h. In using the additive, the cement:additive ratio should be approximately 47 lb to 17.5 lb.
- i. Sixty-five pounds of additive will equal 0.78 cu ft when sand is added (apparently one-third part of sand by volume based on the volume of the additive).

j. When using the additive, it is recommended that to 1 lb of additive, 2-1/3 lb of gray portland cement and 1-1/2 lb of medium grain, dry sand be added.

Scope of Investigation

3. The investigation involved an evaluation of the basic properties of the material by petrographic and X-ray diffraction examination and chemical analysis. Physical tests for time of setting, compressive strength of cubes at 1 hr, 24 hr, 7 days, and 28 days, and for sulfate resistance were made.

PART II: MATERIALS

Proprietary Material

4. Three samples of the proprietary material were received from the manufacturer. The first sample, consisting of a 1-gal container of "field mix" (AD-110), was received on 20 April 1959; the second sample, consisting of a 1-gal container of the "additive" (AD-110-A), was received on 23 November 1959; and the third sample, consisting of a 5-gal container of the additive (AD-110-A(2)), was received on 15 June 1960.

Cement

5. Type I portland cement (RC-449) was used in the mixture from which samples for the compressive strength and time of setting tests were obtained. A Type I portland cement (RC-167) with a tricalcium aluminate (C_3A) content of 12.0% and a Type II portland cement (RC-452) with a C_3A content of 6.0% were used for the sulfate-resistance test specimens.

Sand

6. The sand used with the additive in preparing samples for the compressive strength tests was a natural siliceous sand graded into two sieve fractions with a specific gravity of 2.61 and an absorption of 0.7%. The sand used for the sulfate-resistance test specimens was graded standard Ottawa sand.

PART III: TESTS AND RESULTS

Petrographic Examination and X-ray Diffraction

Test procedure

7. "Field mix." Small samples of the "field mix" (AD-110) were examined under the stereomicroscope. An X-ray diffraction chart of the "field mix" was made at 2 deg per min, using copper radiation filtered through two layers of nickel foil, at 50 KVP and 16 ma. Additional X-ray examinations were made of samples of the "field mix" prepared in the following ways:

a. The material passing the No. 100 sieve was separated using a liquid with a specific gravity of 2.75 and centrifuging to obtain a heavy and a light fraction. The two fractions were washed in acetone and air-dried; each was ground in an agate mortar, then packed in a sample holder so as to reduce preferred orientation.

b. X-ray diffraction patterns of each sample were obtained under the following conditions: copper radiation filtered through two layers of nickel foil, at 50 KVP and 16 ma, target angle 4 deg, side port; slit system: from 10 to 20 deg 2-theta, beam 1 Soller 3 detector 0.2; beyond 20 deg 2-theta, beam 3 Soller MR detector 0.2; ratemeter range, log 4000; time constant, 30 sec, 7.5 sec, N; input sensitivity, 3.5 volts; reverter in at 96%; speed 0.2 deg per min.

8. Additive. The additive was examined under the same X-ray diffraction conditions as those listed in the preceding paragraph, except that the sample was tightly packed in the holder.

Composition of the "field mix"

9. The manufacturer's description said that the "field mix" contained 50% portland cement, 32% sand, and 18% additive. The stereomicroscope and X-ray examinations gave results that were in general qualitative agreement with these proportions, although no quantitative results were obtained. The sand consisted principally of quartz; the portland cement contained a relatively large amount of C_3A, and the pattern appeared to be that of a Type I or Type III cement.

Composition of the additive

10. The additive consisted of plaster of Paris and kaolinite with a small amount of quartz, which was probably an impurity of the clay, and a small amount of anhydrite, assumed to be an impurity of the plaster. While

it seems possible that some accelerator or set controller for the plaster is included in the additive, it was not identified in the X-ray patterns. The role of the kaolinite may be to improve the handling properties of the mixture while it is plastic; presumably its function after the plaster has set and after the concrete or mortar containing the additive has hydrated is as an inert aggregate.

Chemical Analysis

11. Based on the results of the petrographic and X-ray diffraction studies, it was decided that a chemical analysis should be conducted of the substances indicated to be present. The chemical analysis was performed on a portion of the first sample of the additive (AD-110-A). The sample for analysis was weighed as received, fused, and analyzed for the several constituents as follows:

Constituents	%	Moles per 100 g of As-Received Samples
Cl	0.15	0.0042
SiO_2	23.69	0.3944
Al_2O_3	20.77	0.2037
CaO	21.06	0.3755
SO_3	23.55	0.2942
Fe_2O_3	0.35	---
H_2O loss at 200 C	3.46	0.1920
H_2O loss at 600 C	10.15	0.5634

The chemical composition of kaolinite is $Al_2O_3.2SiO_2.2H_2O$. Since 0.3944 moles of SiO_2 were found in the additive, the Al_2O_3 content of the additive, if it were all kaolinite, should be 0.1972. Apparently there is an excess 0.0065 moles of Al_2O_3 not introduced by the kaolinite. The additive also contains 0.0813 moles of CaO in excess of the amount needed for the plaster* component of the additive.

Based on these results it is evident that:

Moles H_2O needed for kaolinite = 0.3944

Moles H_2O needed for plaster = 0.1471

Total moles H_2O needed = 0.5415

$0.5634 - 0.5415 = 0.0219$ excess moles of H_2O

$0.0065 \times 101.96 = 0.66\%$ excess Al_2O_3

$0.0813 \times 56.08 = 4.56\%$ excess CaO

$0.0219 \times 18 = 0.39\%$ excess H_2O

* Calcium sulfate hemihydrate (plaster of Paris).

12. Next, two additional samples of the additive (AD-110-A) were weighed, moisture loss at 600 C determined, and two 1-g samples of the dried material were treated with 400 ml of H_2O and 5 ml of HCl. Sample 1 was agitated at room temperature for 4 hr, allowed to stand overnight, and filtered; sample 2 was digested on the steam bath for 4 hr and filtered. Aliquots of the filtrate were analyzed; the results of the analyses are listed below:

Constituent	Per Cent by Weight	
	Sample 1	Sample 2
Residue	47.26	---
SiO_2	1.00	3.31
R_2O_3*	1.64	20.70
SO_3	23.58	23.57
CaO	20.90	20.51**
H_2O loss at 600 C	9.91	9.78

* R represents all the constituents rendered insoluble by treatment with ammonium hydroxide.
** Value a little low because a small amount was lost.

13. It appears that all the calcium- and sulfate-bearing compounds found in the additive are soluble in dilute HCl solutions. Some of the silica is soluble; a small amount of Al_2O_3 is soluble in cold dilute HCl solution, and most all of the Al_2O_3 is soluble in hot dilute HCl solution.

14. No explanation of the excess CaO is apparent on the basis of the theoretical molecular weights of kaolinite and plaster. It would appear that there is additional calcium in the additive that is not in the form of calcium sulfate hemihydrate (plaster of Paris).

Physical Tests

Testing program

15. Testing was directed toward determining the basic properties and characteristics of the proprietary material. The "field mix" was used for

familiarization with the material and mixing procedures, for petrographic examination, and for compressive strength and time-of-setting determinations. The additive was used in chemical analysis and petrographic examinations and then combined with laboratory cement and sand in mixtures which were used for making compressive strength, time-of-setting, and sulfate-resistance test specimens.

"Field mix"

16. The first time-of-setting and compressive strength tests of the "field mix" were made using a mixture containing four parts by weight of sample AD-110 (3000 g) and 1-1/2 parts distilled water (1125 g) mixed in a steel bowl with a steel spoon until a well-mixed paste was obtained. This mixture had not reached Gillmore initial set in 2 hr 51 min. It then being the close of the work day, no further time-of-setting observations were made for 15-1/2 hr. At that time it was found that final set had occurred. Two-inch cubes were made from this paste and tested at the following ages with results as indicated:

Age	Compressive Strength, Avg for 3 Cubes, psi
1 hr	20
24 hr	785
7 days	1215
28 days	2415

17. With the remaining 950 g of field mixture, two mortars of variable consistency were made and tested for setting time and strength to the extent possible with the limited amount of material.

a. One mortar was made by mixing 450 g of AD-110 with 155 ml of water and troweling the material into the water until it was thoroughly mixed. This mixture was semifluid in consistency, that is, not cohesive enough to be readily formed into any definite shape without being confined in a mold. A pat was made, and time of set was determined by Gillmore needles. Initial set was reached in 9 min and final set in 4 hr 45 min. Since the material was so fluid and stuck to the mold and trowel, not enough of it was left after making the time-of-setting pat for making a cube.

b. Another mortar was made using 450 g of AD-110 and 106 ml of water. This mortar had the approximate consistency of a normal cement paste. The material was worked into the water until thoroughly mixed. A pat was made and tested for

> Gillmore time of setting. Initial set was reached in 6 min and final set in 13 min. A 2-in. cube was made and tested for compressive strength at 1 hr after mixing; the strength was 102 psi.

18. It is not known why the first mixture tested failed to reach initial set in 2 hr 50 min and the two subsequently tested portions of the same sample reached initial set in 9 min and 6 min, respectively, or why the final setting time of the two subsequently tested samples was 4 hr 45 min in one case and only 13 min in the other.

Additive

19. Time-of-setting and compressive strength tests. For these tests a batch using additive sample AD-110-A was made with a Type I portland cement (RC-449) and a natural siliceous sand (CRD-S-4(15)). The sand consisted of equal parts of two sieve fractions: that passing a No. 16 and retained on a No. 30 sieve; and that passing a No. 30 and retained on a No. 50 sieve. The proportions used were:

Material	Amount, lb	Per Cent by Weight
Additive (AD-110-A)	2.00	16.5
Portland cement (RC-449)	4.67	38.5
Sand (No. 16 to No. 30)	1.50	24.8
Sand (No. 30 to No. 50)	1.50	
Water	2.45	20.2
	12.12	100.0

20. Generally the mixing procedure recommended by the manufacturer was followed. First, all of the materials, except the water, were blended and approximately one-third of this blend was set aside. The water was then added to the larger portion, giving a relatively wet mixture. The dry portion was added gradually and mixed until all constituents appeared to be thoroughly blended. The recommended procedure referred to "white streaks... on the exposed face of the mix" when proper mixing had been obtained, but the streaks were not pronounced enough to use as a guide. When visual observation indicated a homogeneous, stiff, hand-placeable substance, mixing was considered to be complete.

21. Two time-of-setting test specimens and four sets of cubes for compressive strength tests were made from the mixture. One

time-of-setting determination was made with the Vicat apparatus (Method CRD-C 222)[3*] and one with the Gillmore needles (Method CRD-C 220).[3] For both methods the initial time of setting was approximately 14 min and the final time approximately 24 min. Three 2-in. cubes, made according to CRD-C 227[3] and cured at 72 to 76 F and over 90% relative humidity, were tested at each of four different ages. The strength results are given below for each age.

Age	Compressive Strength, Average for 3 Cubes, psi
1 hr	105
24 hr	2310
7 days	4260
28 days	5570

22. Sulfate resistance. The effect of the additive on the sulfate resistance of mortars was evaluated by two methods. In one method,[4] lean mortar bars were made with a high C_3A cement, without and with the additive (mixtures 1 and 2), and were stored in a sulfate solution. These mixtures are described in table 1. In the second method,[1] mortar bars were made with calcium sulfate and the additive (or plaster of Paris instead of the additive) incorporated in the mixtures (mixtures 3-7), and were stored in water. These five mixtures are also described in table 1; their principal features were:

a. Mixture 3 was the basic mix called for in the ASTM test procedure.[1]

b. Mixture 4 was proportioned to have a cement:additive ratio as recommended by the manufacturer and flow approximating that of mixture 3. The additive was prehydrated, as was the plaster when it was used, to avoid premature stiffening.

c. Mixture 5 was proportioned the same as mixture 4 with plaster in place of the additive.

d. Mixtures 6 and 7 were made using the manufacturer's recommended proportions and mixing procedure, but mix 6 contained the same cement used in mixes 1-5 (which contained 12.0% C_3A) whereas mixture 7 contained the Type II cement having a C_3A content of 6.0% as calculated from chemical analysis. Both mixtures had the consistency of putty or modeling clay.

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* Raised numbers refer to similarly numbered items in the list of references.

23. In all tests, the amount of expansion was taken as a measure of the sulfate susceptibility of a mixture. As seen in table 2, the lean mortar bars with the additive (mixture 2) expanded approximately three times as much as the mortar without the additive (mixture 1) during 28 days of storage in sulfate solution. This indicates that the presence of the sulfate-containing additive accelerates expansion of a high C_3A cement mortar over the rate experienced with a similar mortar which must derive the sulfate from the solution in which the bars are stored in order to react with the aluminate.

24. In the added-sulfate test, mixtures 3, 4, and 5 expanded almost equally up to 28 days, when the readings were stopped. As shown by table 2, mixture 6 with the higher C_3A cement expanded appreciably more than mixture 7 with the lower C_3A cement. There was no noticeable disintegration of any of the bars at 28 days age. These data confirm the indications of the chemical and petrographic analyses and the lean mortar-bar test that the additive contains soluble sulfate as a major constituent, and that the sulfate so contained performs similarly to sulfate in external solution, or added to mortars, in producing sulfate-attack expansion proportionate to the C_3A content of the cement employed.

25. Any mortar bar that expands as much as 0.1% may be assumed to have undergone excessive expansion and to have manifested whatever phenomenon caused the expansion to a deleterious extent. The data from the added-sulfate test[1] indicate that mortars made with cements having C_3A contents comparable to RC-167, i.e. 11 to 12%, develop expansions of the order of 0.1% at 28 days. For Type V cements, in which the C_3A content is required to be less than 5.0%, the expansion at 28 days apparently should not exceed 0.05%. Applying these limits to the data developed here, it is seen that mixtures 3, 4, and 5 all show excessive expansion. Mixtures 6 and 7 exceed the limits for a sulfate-resistant cement.

26. Concrete construction exposed to external sulfate attack, as for example in marine exposures, should contain both relatively low C_3A cements and low-permeability mixtures so that the potential expansion due to the formation of calcium sulfoaluminate will be low and the rate at which sulfate permeates the concrete from the exposure will also be low. Mixtures used in concrete construction to be exposed to penetration of moisture--

rain, ground water, river water, etc.--should not contain soluble sulfates unless the C_3A content of the cement is exceedingly low. Therefore, it is indicated that the additive under study--since it contains a large proportion of soluble sulfates--should not be used in concrete in which the cement contains appreciable quantities of C_3A where the construction will be exposed to moisture. The combination of the additive with a cement of relatively high C_3A content and the exposure of the resulting paste in mortar or concrete to a moist environment may be expected to induce excessive expansion. If the moisture to which the paste is exposed contains dissolved sulfates, the expansion may be greater than would otherwise be the case, if the amount of sulfate provided by the additive is insufficient to convert all the C_3A in the cement to calcium sulfoaluminate. If sufficient sulfate is provided by the additive to react with all the C_3A in the cement, the question of whether the exposure involves fresh water or sulfate solution should have little effect on the magnitude of the expansion.

PART IV: CONCLUDING STATEMENT

27. Based on the results obtained in this investigation, it is concluded that the additive (AD-110-A) could have practical applications in specialized types of repair or construction where the situation calls for a quick-setting, hand-placeable, cementitious mixture. However, it is indicated that the material should not be used where it might be exposed to moisture after use unless its use is limited to mixtures containing sulfate-resistant cement (Type V).

REFERENCES

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2. "Here's a new way to make old pier piles good as new." Engineering News-Record, vol 162, No. 8 (26 February 1959), pp 40-41.

3. U. S. Army Engineer Waterways Experiment Station, CE, Handbook for Concrete and Cement, with quarterly supplements. Vicksburg, Miss., 1949.

4. Wolochow, David, "Determination of the sulfate resistance of portland cement; Appendix A, A lean mortar bar test for sulfate resistance of portland cements." American Society for Testing Materials Proceedings, vol 52 (1952), pp 264-265.

Table 1

Sulfate-Resistant Mixtures

Mixture No.	Test	Cement* Type	Cement* g	Additive AD-110-A(2) g	Ottawa Sand g	Plaster g	Water g	Flow** %	Ratio of Water to Cementitious Material by Wt
1	Lean bars[4†]	RC-167	300	---	1200	---	225	105	0.75
2	Lean bars[4]	RC-167	210	90	1200	---	250	103	0.83
3	Added sulfate[1]	RC-167	360	---	1100	40	216	97	0.54
4	Added sulfate[1]	RC-167	280	120	1100	---	300	132	0.75
5	Added sulfate[1]	RC-167	280	---	1100	120	300	106	0.75
6	Added sulfate[1]	RC-167	725	290	435	---	447	---	0.44
7	Added sulfate[1]	RC-452	725	290	435	---	400	---	0.39

* C_3A content of RC-167, 12.0%, calculated from chemical analysis.
C_3A content of RC-452, 6.0%, calculated from chemical analysis.

** Made according to CRD-C 210-57 with 25 drops in 15 sec.

† Raised numbers refer to similarly numbered items in the list of references.

Table 2

Results of Sulfate-Resistance Tests

Mixture No.	Round No.	Bar No.	2-Day Weight g	% Expansion at 7 Days	14 Days	21 Days	28 Days
1	1	1	382.8		0.005	0.007	0.017
		2	383.0		0.007	0.010	0.018
	2	1	378.2		0.009	0.018	0.037
		2	382.0		0.010	0.019	0.037
		Avg	381.5		0.008	0.014	0.027
2	1	1	383.1		0.033	0.056	0.073
		2	380.5		0.033	0.056	0.076
	2	1	385.0		0.035	0.053	0.073
		2	388.3		0.033	0.056	0.071
		Avg	384.2		0.034	0.055	0.073
3	1	1		0.043	0.065	0.083	0.104
		2		0.046	0.070	0.087	0.105
		3		0.043	0.067	0.084	0.106
	2	1		0.044	0.067	0.083	0.103
		2		0.045	0.070	0.085	0.105
		3		0.046	0.071	0.087	0.106
		Avg		0.045	0.068	0.085	0.105
4	1	1		0.055	0.078	0.094	0.112
		2		0.049	0.070	0.087	0.110
		3		0.061	0.084	0.101	0.123
	2	1		0.055	0.080	0.095	0.113
		2		0.052	0.075	0.091	0.114
		3		0.054	0.078	0.094	0.112
		Avg		0.054	0.078	0.094	0.114
5	1	1		0.040	0.061	0.075	0.092
		2		0.036	0.056	0.085	0.110
		3		0.038	0.058	0.072	0.090
	2	1		0.042	0.063	0.079	0.096
		2		0.044	0.063	0.077	0.096
		3		0.043	0.062	0.074	0.092
		Avg		0.041	0.061	0.077	0.096
6	1	1		0.083	0.109	0.134	0.161
		2		0.086	0.113	0.137	0.160
		3		0.084	0.112	0.138	0.162
		Avg		0.084	0.111	0.136	0.161
7	1	1		0.056	0.071	0.083	0.095
		2		0.053	0.067	0.078	0.089
		3		0.053	0.067	0.079	0.090
		Avg		0.054	0.068	0.080	0.091

Note: Initial reading taken at 7 days for mixtures 1 and 2 and at 1 day for others.